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Catalytic Alkenylation of Phenylpyridines with Terminal Alkynes by a [12]Metallacrown-6 Ruthenium(II) Compound

Ming-Hua Xie, Miao Wang, and Chuan-De Wu*

Department of Chemistry, Zhejiang University, Hangzhou 310027, People's Republic of China

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Two new [12]metallacrown-6 compounds, $[M^{II}_6(SMe)_{12}]$ [M = Ru (**1**), Zn (**2**)], were constructed from a dimethyl sulfoxide decomposed methylthiol product to doubly bridged metal centers. The Ru^{II} compound can prompt alkenylation reactions of phenylpyridines with alkynes to generate monoalkenylated arylpyridines in moderate yields with high regioselectivity and stereoselectivity.

In the past few years, considerable interest has been focused on the construction of metallacrown compounds for aesthetically topological architectures and potential applications in various research fields, such as electronics, separation, and magnetic materials.[1−4] The ubiquitous S-bridged metal rings exhibit fascinating cluster configurations by forming the edge-shared coordination square plane $\{MS_4\}$. Most hexanuclear metallacrown clusters formulated as $[M_6(SR)_{12}]$ are nickel and palladium compounds, which are composed of 12 thiolate ligands and 6 metal cations with 6 metal centers in a coplane conformation.[4−6]

During our course in the synthesis of functionalized metal−organic frameworks, we got two unexpected compounds with the composition $[M^{II}_6(SMe)_{12}]$ [M = Ru (**1**), Zn (**2**)]. At the beginning, both compounds were synthesized in very low yields by heating a mixture of $RuCl_3$ or $ZnCl_2$ and 2,2′-bipyridine-5,5′-dicarboxylic acid in dimethyl sulfoxide (DMSO) and methanol (MeOH) at 65 °C in a capped vial for 1 week. However, without the addition of an organic ligand, both compounds also formed after a few days.[7] It is known that DMSO can be decomposed into sulfur dioxide, formaldehyde, methylthiol, methyl thioether, etc.[8] Thus, the bridging methylthiol ligand should be a decomposed product from a DMSO solvent. Subsequently, the reduced Ru or Zn atoms reacted with the decomposed methylthiol product to form the two hexanuclear cyclic metal thiolates.

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*To whom correspondence should be addressed. E-mail: cdwu@zju.edu.cn.

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(7) **Synthesis of $\{Ru_6(SMe)_{12}\}$ (1).** Heating a mixture of $RuCl_3$ (41.4 mg, 0.2 mmol), 2,2′-bipyridine-5,5′-dicarboxylic acid (24.4 mg, 0.1 mmol), 36.5% HCl (0.05 mL), MeOH (2 mL), and DMSO (1 mL) at 65 °C in a capped vial afforded brown crystals of **1** after 1 week (yield 8.9% based on Ru). Without the addition of 2,2′-bipyridine-5,5′-dicarboxylic acid, compound **1** can be synthesized according to the following procedure: after heating of a mixture of $RuCl_3$ (41.4 mg, 0.2 mmol), 36.5% HCl (0.05 mL), MeOH (2 mL), and DMSO (1 mL) at 85 °C in a open vial for 1 week, 2 mL of MeOH was added, which produced brown crystals of compound **1** at room temperature after 2 days (yield 87% based on Ru). The brown crystals were filtered, washed with EtOH and Et_2O, and dried at room temperature. Anal. Calcd for $C_{12}H_{36}Ru_6S_{12}$: H, 3.10; C, 12.30; S, 32.84. Found: H, 3.15; C, 12.43; S, 31.96. ^1H NMR (500 MHz, $CDCl_3$): δ 2.62(s). ^{13}C NMR (125 MHz, $CDCl_3$): δ 39.1. IR (KBr pellet, ν/cm^{-1}): 1630 m, 1406 m, 1312 m, 1100 s, 935 s, 679 m. **Synthesis of $\{Zn_6(SMe)_{12}\}$ (2).** The synthesis procedure is similar to that of **1**, except that $RuCl_3$ was replaced by $ZnCl_2$ (27.2 mg, 0.2 mmol; yield 6.1% based on Zn). Without the addition of an 2,2′-bipyridine-5,5′-dicarboxylic acid ligand, compound **2** also formed as brown crystals after 1 week according to the synthesis procedure of **1** (yield 65% based on Zn). Anal. Calcd for $C_{12}H_{36}Zn_6S_{12}$: H, 3.79; C, 15.05; S, 40.18. Found: H, 3.85; C, 15.32; S, 39.76. ^1H NMR (500 MHz, $CDCl_3$): δ 2.69(s). ^{13}C NMR (125 MHz, $CDCl_3$): δ 40.2. IR (KBr pellet, ν/cm^{-1}): 1637 m, 1434 m, 1317 m, 1021 s, 953 s, 708 m, 447 m.

(8) http://www.arkema-inc.com/literature/pdf/363.pdf.

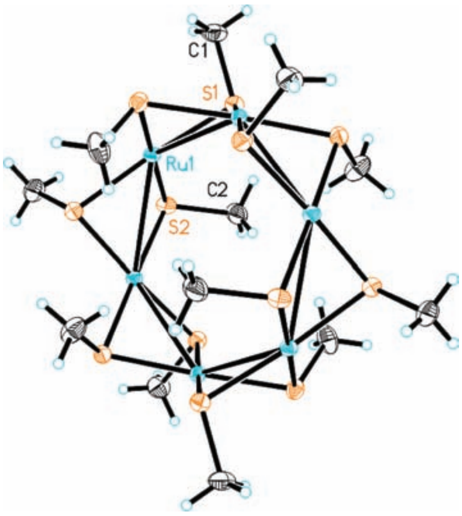

Figure 1. ORTEP representation of the molecular structure of **1**.

A single-crystal X-ray structural study revealed that compound **1** crystallizes in the trigonal $R\overline{3}$ space group.[9] It is a hexagonal $\{Ru_6(SMe)_{12}\}$ framework in the [12]metallacrown-6 configuration (Figure 1), which is similar to that of the previously reported complexes of $[\{M(\mu_2\text{-}SR)_2\}_6]$ (M = Ni, Pd).[4−6] There are one Ru^{II} atom and two deprotonated MeS ligands in each asymmetric unit. Each Ru^{II} atom coordinates to four S atoms from four MeS units [Ru−S = 2.329(1)−2.339(1) Å] in a distorted square-planar geometry. The RuS_4 units are further doubly bridged by S atoms to form a six-membered ruthenium metallacrown with an average Ru···Ru distance of 3.128(1) Å and a vertex angle of 120°. By careful inspection of the crystal structure, we found that there is no significant supramolecular interaction other than van der Waals contacts between these clustered rings.

To investigate whether the solid-state structure of **1** is retained in solution, ^1H and ^{13}C NMR spectra were recorded in a $CDCl_3$ solution. The NMR spectra of **1** present simple patterns, which suggest that there is only one type of ligand present in the solution. In the UV/vis spectrum, three main peaks (365, 316, and 249 nm) were observed, which are assigned to the ligand-to-metal charge-transfer transition (365 nm), metal-centered transition (316 nm), and ligand-centered transition (249 nm).[4a]

Compound **2** displays geometric features identical with those of compound **1**, which crystallizes in the monoclinic $P2_1/n$ space group.[9] There are three Zn^{II} atoms and six deprotonated MeS ligands in each asymmetric unit (Figure 2). Each Zn^{II} atom tetracoordinates to four S atoms from four MeS units [Zn−S = 2.324(4)−2.341(4) Å] in a distorted square-planar geometry. The $[ZnS_4]$ units are further doubly bridged by S atoms to form a [12]metallacrown-6 with an average Zn···Zn distance of 3.019(2) Å and an average vertex angle of 120.0(1)°. Different from compound **1**, the slightly deviated vertex angles from the idealized hexagon value for compound **2** arise because compound **2** crystallizes in the monoclinic $P2_1/n$ space group, while compound **1** crystallizes in the trigonal $R\overline{3}$ space group to idealized hexagon symmetry to Ru atoms. Different from **1**, there are relatively strong S···S interactions between the ring clusters [S···S = 3.43(4) Å] in order to join the cluster units to form a one-dimensional linear supramolecular framework (Figure 3), which is further stacked together via van der Waals interactions. The structure of **2** should be different from the previously reported $[Zn(SMe)_2]_n$ because it is insoluble in common organic solvents, which was suggested as a MeS-bridged polymeric structure.[10] The different results might be attributed to the different synthetic routes.

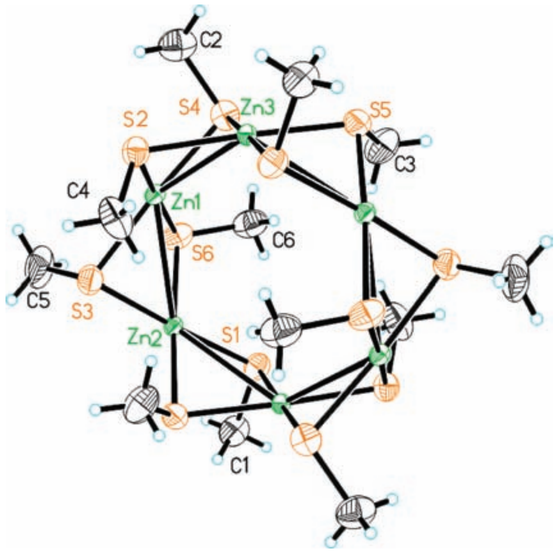

Figure 2. ORTEP representation of the molecular structure of **2**.

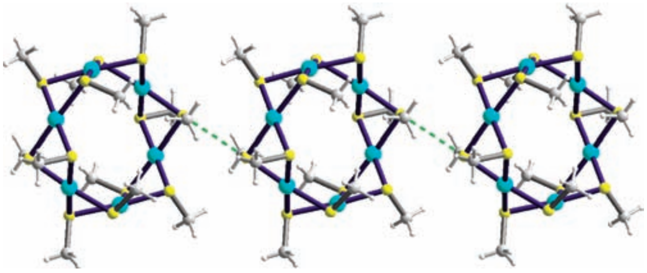

Figure 3. View of the linear supermolecular network in **2** linked by S···S short contacts. The color code is as follows: Zn, cyan; S, yellow; C, light gray; H, white.

Recent research work has shown that C−H bond activation by transition-metal complexes was one of the important methods for the C−C bond coupling reaction, and ruthenium compounds have been used as catalysts for many important coupling reactions.[11] To date, the only example of alkenylation of arylpyridines in chelation-assisted C−H bond

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[9] **Crystal data for 1**: $C_{12}H_{36}Ru_6S_{12}$, M_r = 1171.55, trigonal, space group $R\overline{3}$, a = 17.815(3) Å, c = 8.786(2) Å, V = 2414.8(7) Å ^{3}, Z = 3, T = 293 K, D_c = 2.417 g cm^{-3}, μ = 3.526 mm^{-1}, $F(000)$ = 1692, GOF = 1.159, 7937 measured reflections, 1225 unique reflections (R_{int} = 0.025). The final R1 = 0.0186, wR2 = 0.0494 for 1151 observed reflections with $I > 2\sigma(I)$ and R1 = 0.0202, wR2 = 0.0499 for all data with 46 parameters. **Crystal data for 2**: $C_{12}H_{36}S_{12}Zn_6$, M_r = 957.35, monoclinic, space group $P2_1/n$, a = 10.030(2) Å, b = 13.156(3) Å, c = 12.529(3) Å, β = 94.81(3)°, V = 1647.5(6) Å ^{3}, Z = 2, T = 293 K, D_c = 1.930 gcm^{-3}, μ = 5.063 mm^{-1}, $F(000)$ = 960, GOF = 1.081, 15 652 measured reflections, 3740 unique reflections (R_{int} = 0.0625). The final R1 = 0.0763, wR2 = 0.2358 for 2618 observed reflections with $I > 2\sigma(I)$ and R1 = 0.1063, wR2 = 0.2752 for all data with 137 parameters.

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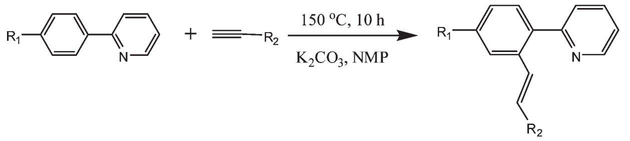
Table 1. Compound **1** Catalyzing the Activation of C−H Bonds[a]



entry	R_1	R_2	yield (%)[b]
1	H	phenyl	57
2	H	*p*-$MeOC_6H_4$	60
3	H	*p*-EtC_6H_4	50
4	H	2-pyridyl	0
5	Me	phenyl	56
6	Me	*p*-$MeOC_6H_4$	62
7	Me	*p*-EtC_6H_4	54
8	Me	2-pyridyl	0

[a] Compound **1** (0.1 mmol), 2-phenylpyridine (1 mmol), phenylacetylene (1.2 mmol), and K_2CO_3 (2 mmol) were mixed in NMP (5 mL), and then the mixture was heated at 150 °C for 10 h. [b] Isolated yields.

activation using terminal alkynes catalyzed by $RuCl_3$ in the presence of benzoyl peroxide or benzoic acid was reported by Zhang and co-workers.[12] The ruthenium metallacrown compound **1** comprises an axial vacant coordination environment, which prompted us to study the catalytic activity using the C−C coupling reaction of phenylpyridines with alkynes as a catalytic test. The reaction of 2-phenylpyridine and phenylacetylene in the presence of compound **1** in *N*-methyl-2-pyrrolidone (NMP) at 150 °C for 10 h gave 57% moderate isolated yield of the alkenylated product 2-(2-styrylphenyl)pyridine (Table 1, entry 1). Gas chromatography−mass spectrometry analysis revealed that only *E* stereoisomers were observed and without double alkenylation, which proved the excellent stereoselectivity and high regioselectivity of the catalyst system. To investigate whether the framework structure of **1** is retained after the catalytic reaction, we have recorded the UV/vis spectrum of recovered **1** in a CH_2Cl_2 solution. The UV/vis spectrum presents patterns similar to those of the original spectrum of **1**, which suggests that the structural motif is maintained during the catalytic process.

Compound **1** can also catalyze the coupling reaction of a variety of terminal alkynes and arylpyridines under the reaction conditions. As shown in Table 1, the electron-donating groups in the arylalkynes and arylpyridines can generate corresponding products to give moderate yields (Table 1, entries 1−3 and 5−7). However, the electron-donating substituents affected the alkenylation processes less efficiently (Table 1, entries 5−7), while the electron-withdrawing substituents on acetylene cannot generate a detectable product (Table 1, entries 4 and 8). Although the catalyst did not generate excellent product yields, the results were valuable compared to the previous report by Zhang et al.[11] They showed that additional adductives of benzoyl peroxide or benzoyl acid played a crucial role for the coupling reaction, while only K_2CO_3 was added to prompt the transformation process in the present work. Also, the reaction mixture was much easier to handle compared to a benzoyl peroxide or benzoyl acid assisted system. We believe that the different catalytic conditions employed contributed to the different catalyst oxidation states (Ru^{II} in the present work and Ru^{III} in the reported work) on the catalytic activity. In the case of the $RuCl_3$-prompted process, additional additives are helpful for proton transformation. On the other hand, they showed that the alkyne with electron-withdrawing substituents also give good alkenylation yields, while the catalytic results are highly affected by different kinds of substituents in the present work. All of these facts suggest that the new catalyst system comprising a low oxidation state of the Ru^{II} atom and a six-nuclear metal-centered framework should undergo a different transformation mechanism.

In summary, we have successfully synthesized two new six-metal-membered metallacrown complexes constructed from a DMSO-decomposed methylthiol product to doubly bridged metal centers. The Ru^{II} compound can catalyze the C−C coupling reaction without the addition of benzoyl peroxide or benzoyl acid to generate alkenylated arylpyridines. We have observed remarkably high regioselectivity and stereoselectivity. Most important of all, the clearly demonstrated crystal structure of **1** provided direct insight for the study of the mechanism toward a detailed understanding of the activation pathways.

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Supporting Information Available: Experimental procedures, analysis data, additional figures, and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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